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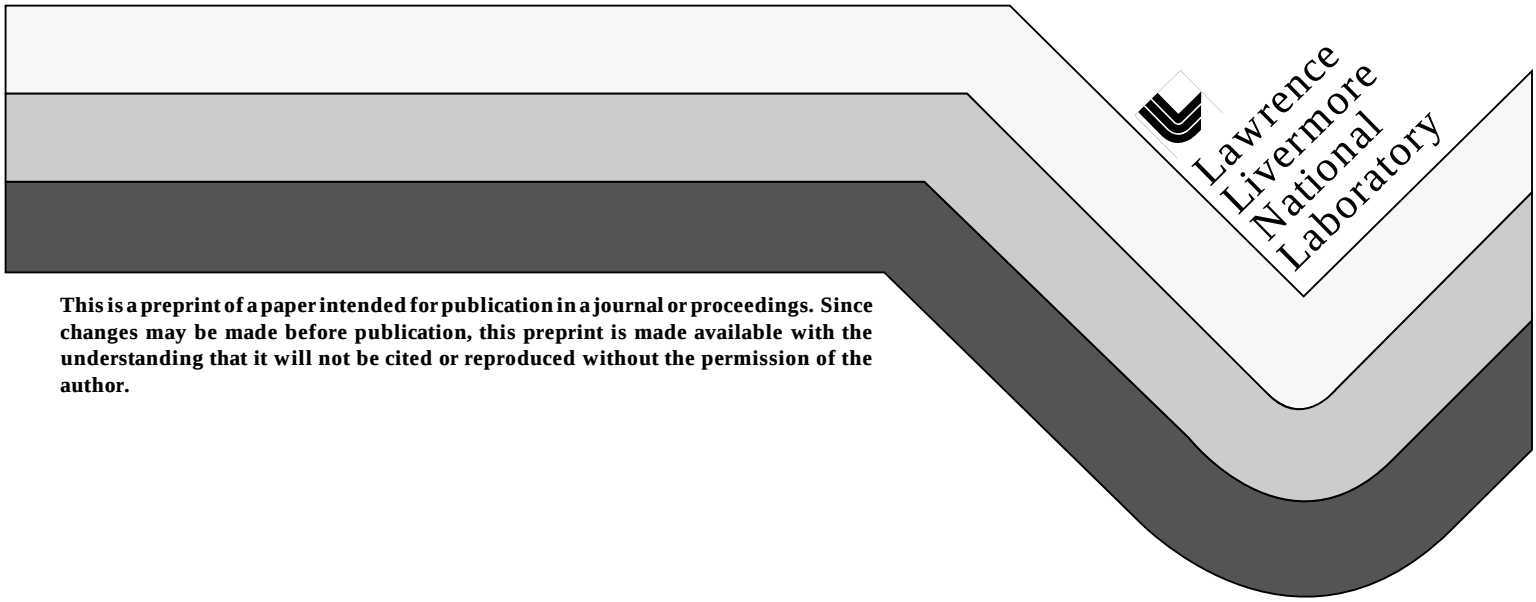

Reaction Progress Pathways for Glass and Spent Fuel Under Unsaturated Conditions

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Introduction

The source term for the release of radionuclides from a nuclear waste repository is the waste form. In order to assess the performance of the repository and the engineered barrier system (EBS) compared to regulations established by the Nuclear Regulatory Commission and the Environmental Protection Agency it is necessary (1) to use available data to place bounding limits on release rates from the EBS, and (2) to develop a mechanistic predictive model of the radionuclide release and validate the model against tests done under a variety of different potential reaction conditions. The problem with (1) is that there is little experience to use when evaluating waste form reaction under unsaturated conditions such that errors in applying expert judgment to the problem may be significant.

The second approach, to test and model the waste form reaction, is a more defensible means of providing input to the prediction of radionuclide release. In this approach, information related to the source term has a technical basis and provides a starting point to make reasonable assumptions for long-term behavior. Key aspects of this approach are an understanding of the reaction progress mechanism and the ability to model the tests using a geochemical code such as EQ3/6. Current knowledge of glass, UO_2, and spent fuel reactions under different conditions are described below.

Reaction Progress - Glass

Figure 1a shows a generalized reaction path for glass reacted under static conditions at 90^{o}C. In this plot the reaction progress is divided into three regions. In the first region, termed initial rate, the reaction is rapid and decreases with time. Bounding initial dissolution rates are a function of glass composition, but are generally about 1 g/m^2/d. As the glass dissolves into solution, chemical feedback

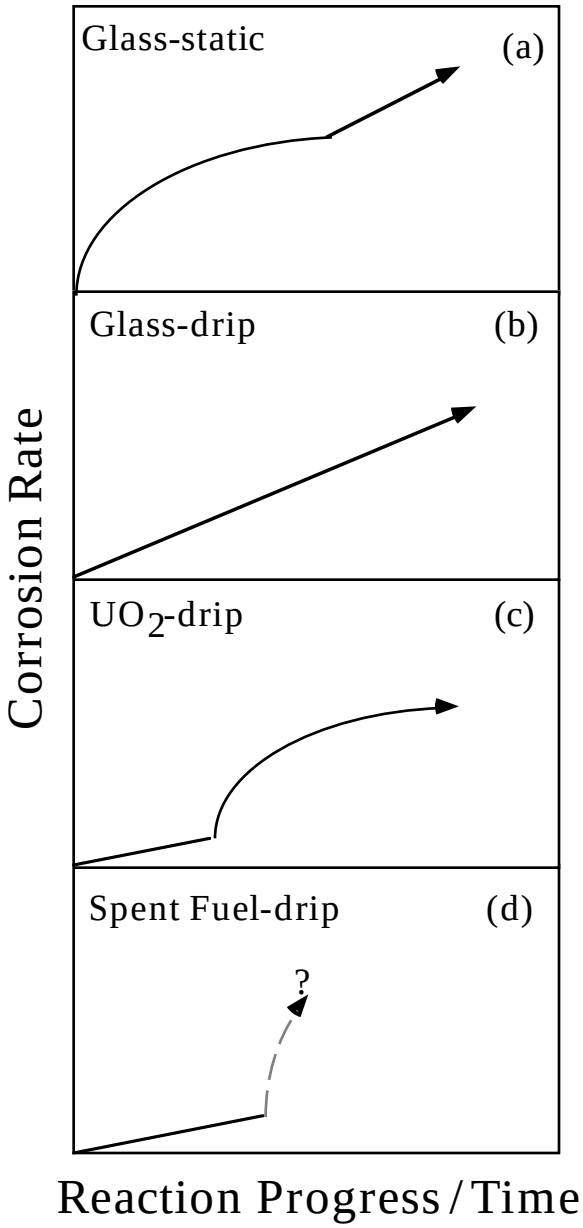

Figure 1. Reaction progress plots for glass, UO_2, and spent fuel.

effects cause the affinity for glass reaction to decrease. This interim dissolution rate is usually about 2 x 10^{-3} g/m^2/d. As the concentration of dissolved components released from the glass increase, nucleation and growth of secondary phases cause the affinity for the dissolution reaction to increase. The reaction rate during this period may be larger than the initial rate. Secondary phases associated with the onset of the final stage include analcime, clinoptilolite, calcium silicates such as gyrolyte and tobermorite, and weeksite, which is a uranium silicate.

The reaction progress plot for glass reacted with intermittent drops of groundwater is shown in Figure 1b. In this case, the reaction progress is nearly linear over the long period of reaction studied. Whereas soluble components of the glass such as boron are released to solution, insoluble components, including the actinide elements, become associated with a surface clay alteration layer. As the water flows over this clay layer it washes portions of the clay layer away from the glass and these layer segments become suspended in solution as colloids. The action of the clay layer forming, spalling from the glass, and reforming proceeds at a steady rate and gives rise to the observed linear release curve.

Reaction Progress - UO_2 and Spent Fuel

The reaction progress plot for UO_2 under conditions of dripping water on a UO_2 monolith is shown in Figure 1c. Results from on-going 8 year duration tests show that initially the release of U to solution is quite slow. However, after about 6 months there is a dramatic increase in release. During this increase in release the formation of secondary mineral phases is observed as the UO_2 is oxidized. The dissolution rate is about 12 $mg/m^2/d$ As the matrix oxidizes, the grain boundaries are dissolved and individual UO_2 grains are released from the matrix. The sequence of uranium bearing phases which covers the UO_2 surface (see Figure 2) form a mat which temporarily inhibits the release of UO_2 grains. The dissolution rate of UO_2 is decreased to about 0.3 $mg/m^2/d$. However, the reaction of the UO_2 continues as evidenced by the continued growth of the surface mat. It is likely that the reaction of the UO_2 matrix will be controlled by the rate at which secondary phases form, which in turn will be dependent on the amount and composition of groundwater that contacts the UO_2. Modeling using EQ3/6 will be used to better understand this process.

The information gained from the reaction of UO_2 takes on paramount importance in light of the results of drip tests that have been performed on spent fuel. A generalized reaction progress plot for spent fuel based on test data obtained over two-year (on-going) tests is shown in Figure 1d. The reaction progress is following the form found for UO_2 but as of yet has shown no tendency for the rate to decrease. Additionally, the sequence of secondary phases that forms appears to be similar to those observed for UO_2. Another major difference between the release of material from UO_2 and spent

fuel is that for spent fuel the release of spent fuel grains is restricted due to a fine filter placed in the test apparatus to support the fuel. Only highly reacted grains can pass through the filter. Those that do are clearly transportable and are counted as released from the fuel.

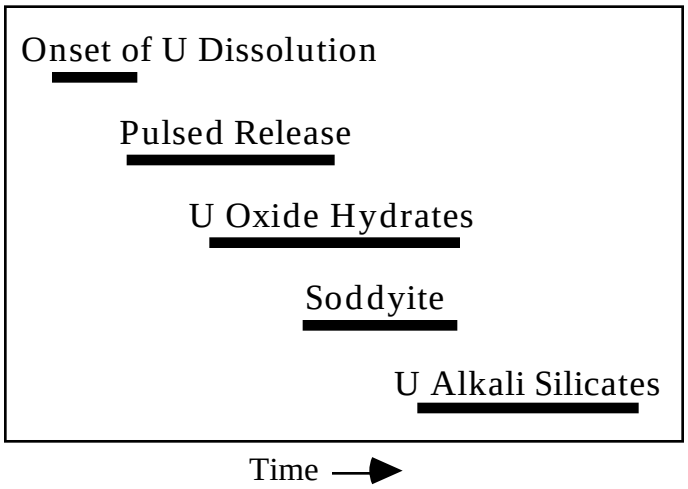

Figure 2. Interpretive paragenetic sequence of the reaction path observed in drip tests performed on UO_2.

Conclusions

The release of radionuclides from both glass, UO_2, and spent fuel can be described by reaction progress plots. These plots provide release information as a function of time and reaction conditions and this information is essential to provide a credible source term to perform assessments of radionuclide release from the EBS and the repository. Because of the unique nature of the unsaturated zone and the lack of experience in dealing with materials performance under the range of conditions expected to be present, it will be possible to generate bounding assumptions regarding waste form reactivity, radionuclide release and transport only by performing a combination of testing and modeling that accounts for conditions relevant to the repository.

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